EPR IMAGING INVESTIGATIONS OF GLASS EPOXY COMPOSITE MATERIALS AND TRACER DIFFUSION IN CERAMICS

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INTRODUCTION

Nondestructive evaluation (NDE) of flaws and defects in non-metallic materials including polymers, ceramics, semiconductors and composites is important for scientists and engineers involved in a wide variety of applications. Magnetic resonance techniques are potentially powerful tools for this purpose. The ability to map out details of internal structure in a noninvasive manner using Nuclear Magnetic Resonance (NMR) has revolutionized diagnostic medicine. Some of the same benefits are realizable for the NDE of solid materials using Electron Paramagnetic Resonance (EPR) and EPR Imaging (EPRI) [1]. This technique has the potential to yield three-dimensional images of manufacturing defects and damage sites in nearly any non-metallic solid.

BACKGROUND

Generally, magnetic resonance spectroscopy relies on the interaction of magnetic moments in a solid with simultaneously applied radio frequency (rf) and spatially uniform magnetic fields. In the more familiar case of NMR, the observable magnetic moments arise from unpaired nuclear moments of the protons and neutrons in the nucleus. In EPR, unpaired valence electrons result in a net magnetic moment and an observable signal. The applied magnetic field induces a splitting of the quantum ground state energy of a magnetic moment (the Zeeman effect) that increases linearly with

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magnetic field. A resonant radio frequency field incident on the sample induces transitions between the energy levels (subject to quantum mechanical selection rules) when the appropriate relationship exists between the frequency of the incident rf and magnetic field strength, given by:

$$\Delta E = h\nu = \mu g H \tag{1}$$

where ΔE is the energy splitting, h is Planck's constant, ν is the frequency of the incident rf, μ is the magnitude of the magnetic moment, g is a numerical factor, and H is the magnitude of the applied resonant magnetic field. A resonance is detected as a peak in the rf power absorption of the sample as the magnetic field is varied. The width of the absorption peak and its spectral location are determined by the physical and chemical environment and the intensity of the absorption peak is directly proportional to the density of magnetic moments in the sample volume.

The chemical and physical environments of microscopic magnetic moments (nuclei or electrons) in solid state materials make them extremely difficult to study by magnetic resonance. The magnetic moments are rigidly held in close physical contact producing strong magnetic interactions and extremely short relaxation times for the excited states observed in magnetic resonance. In the frequency domain, the short relaxation times transform into very broad (sometimes unobservable) resonance lines. Efforts to overcome these limitations center on the development of line narrowing magnetic resonance pulse sequences and on mathematical deconvolution procedures to artificially narrow spectral features (*vide infra*).

EPR is suited to the investigation of phenomena which result in the occurrence of stable paramagnetic centers in a material. Generally, these centers result from broken or dangling chemical bonds, transition metal or rare earth ions or stable free radical compounds. In fact, many of the causes of inferior properties in solid state materials result in observable EPR signals. Processes that result in broken or dangling bonds include radiation damage, mechanical stress, and magnetic sites due to microscopic vacancies or macroscopic voids in the material. Often these primary paramagnetic states are short lived but the final product of their decay frequently results in a stable oxygen containing specie (such as a peroxy free radical) that is paramagnetic. Many impurities present in engineering materials are transition metal or rare earth ions that may be either uniformly dispersed in the parent matrix or localized at features such as voids and inclusions in the material. Signals arising from such impurities can be usefully exploited in EPR. Finally, stable free radical organic compounds can be intentionally doped into otherwise diamagnetic substances to artificially create EPR active sites. Such paramagnetic tracers can be profitably employed to indicate diffusion in porous materials such as ceramics (*vide infra*).

EPR IMAGING: METHOD

As first described by Lauterbur [2], the application of magnetic field gradients to the otherwise uniform magnetic field employed in magnetic resonance spectroscopy encode spatial information onto the signal. With the proper combination of magnetic field gradients, the magnetic moment density throughout a specimen can be experimentally determined. The spatial resolution obtainable in a magnetic resonance

imaging experiment (Δx) is directly proportional to the width of the resonance line (ΔH) and inversely proportional to the magnetic field gradient strength. To record the highest quality images requires an intense, narrow signal and large magnetic field gradients. Narrow, intense resonances are easily obtainable in biological systems due to the superior spectral properties of the proton of water in the liquid phase. These ideal spectral characteristics are completely absent in solid state materials. For certain systems, however, magnetic resonance signals narrow and intense enough to obtain good quality images are observed.

For the EPRI experiments reported here a modified Varian E-12 X-band EPR spectrometer is employed. This spectrometer uses a cw monochromatic microwave excitation and a spatially uniform magnetic field that is temporally varied to record a spectrum. The spatially uniform field is modulated at 100 kHz, phase sensitive detection is employed and the signal is recorded as the first derivative of absorption. The magnetic field gradients are applied by a combination of computer controlled counterwound Helmholz coils and Lewis coils. The microwave frequency is typically 9.4 GHz, the spatially uniform magnetic field ranges from 0-10 kG, and the magnetic field gradients have maximal values of 20 G/mm. Two and three dimensional images require rotation of either the sample or the direction of the net magnetic field gradient.

To demonstrate the EPRI technique and the applicability of the Fourier deconvolution method, a simple magnetic phantom was constructed. This sample nominally consisted of two dots (approximately 0.3 mm wide) of the solid-state organic free radical compound denoted as DPPH [3] mounted on a quartz rod (separation between the dots was approximately 2.1 mm). This compound has the intense, narrow EPR line necessary for EPRI studies. The sequence of Figure 1 illustrates the experimental procedure used to generate a spectrally deconvolved EPR image.

The top display of Figure 1 shows the EPR signal of the test sample in a spatially uniform magnetic field. The next plot shows the effect of a magnetic field gradient applied along the axis of maximum separation of the DPPH spots. The signal becomes sensitive to the separation of the magnetic spins on the sample probe. The separation between the peaks is directly related to the separation of the spins on the sample projected onto the gradient axis. The desired result from this experiment is a one dimensional image of the spin density at a particular angle of magnetic field gradient. Mathematically, the spectrum obtained with a field gradient applied is a convolution of the spectrum in a uniform magnetic field and the one dimensional projection of the spin density, i.e.

$$S_g(h) = \int_{-\infty} S_0(h-h')\rho(h')dh' \tag{2}$$

where $S_g(h)$ is the spectrum obtained with a magnetic field gradient, $S_0(h-h')$ is the spectrum in a spatially uniform field and $\rho(h')$ is the spin density along the gradient direction. Fourier theory provide a means of deconvolving the spin density from the measured spectra by taking the inverse Fourier transform of the quotient of the Fourier transforms of $S_g(h)$ and $S_0(h)$,

$$\rho(h) = \mathcal{F}^{-1}\left\{\frac{\mathcal{F}\{S_g(h)\}}{\mathcal{F}\{S_0(h)\}}\right\} \tag{3}.$$

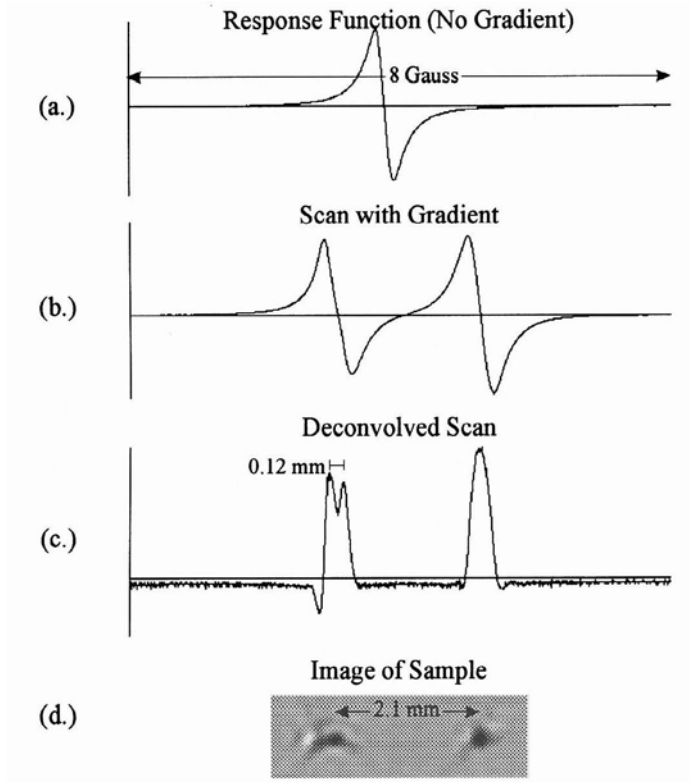

Figure 1. Steps involved in the EPRI technique. Part (a) shows the measured first-derivative of the DPPH absorption line. Part (b) shows a scan with a magnetic field gradient applied. A spin-density projection along the gradient axis, (c), is recovered by deconvolving (b) with (a). Part (d) shows a filtered back projection image created with 36 scans evenly spaced over 180 degrees.

This quantity is shown in the third part of Figure 1 and is the desired one dimensional image of the sample along the direction of the applied gradient. The effect of the deconvolution procedure is to mathematically narrow the linewidth of the EPR signal and to enhance the resolution. An indication of the resolution of the technique is evident in the left hand peak of the one dimensional image. The peak is split into two peaks separated by 120 microns. Optical examination of the sample showed that the DPPH dot responsible for the peak was actually two smaller dots separated by this distance.

A two dimensional image is obtained by taking a series of one dimensional images for a number of angles relative to the field gradient axis and then combining them using filtered back projection techniques (equivalent to those used in computer aided tomography). The result of the application of this procedure, using 36 projections at 5 degree intervals, to the spin phantom sample is shown at the bottom of Figure 1. This general procedure can be applied to conduct EPRI studies on a wide variety of engineering solids.

To demonstrate the feasibility of generating high-quality two-dimensional EPR images of solids, two different classes of materials were studied; a glass epoxy composite and a silica based ceramic. The EPR spectrum of the composite material shows many features across a broad spectral range (Figure 2) while that of the ceramic had no intrinsic EPR signal. These two samples provided excellent examples of two different imaging schemes that have been developed over the course of this study.

The glass epoxy specimen presented a rich EPR spectrum across a broad range (Figure 2). Several features in the spectrum were narrow and intense enough to obtain useful images. The narrowest feature of the spectrum was 20 G wide and was located near 3400 G. Given the position of the resonance, the magnetic specie responsible for this line in the EPR spectrum was likely due to a stable organic free radical formed during the cure of the epoxy. The EPRI system was focussed on this spectral line and two dimensional images were obtained of a rectangular composite sample 6.3 mm by 6.3 mm. The sample was 3 mm thick and had circular hole 1.9 mm in diameter at its center. The image (Figure 3) was obtained from 18 equally spaced scans over 360 degrees with an applied gradient of 20 G/cm and clearly indicated the hole in the center of the composite sample. The overall rectangular shape of the specimen is evident although the edges are not sharp. The lack of fidelity of the image is due to the breadth of the EPR line used to generate the image and could be improved somewhat by

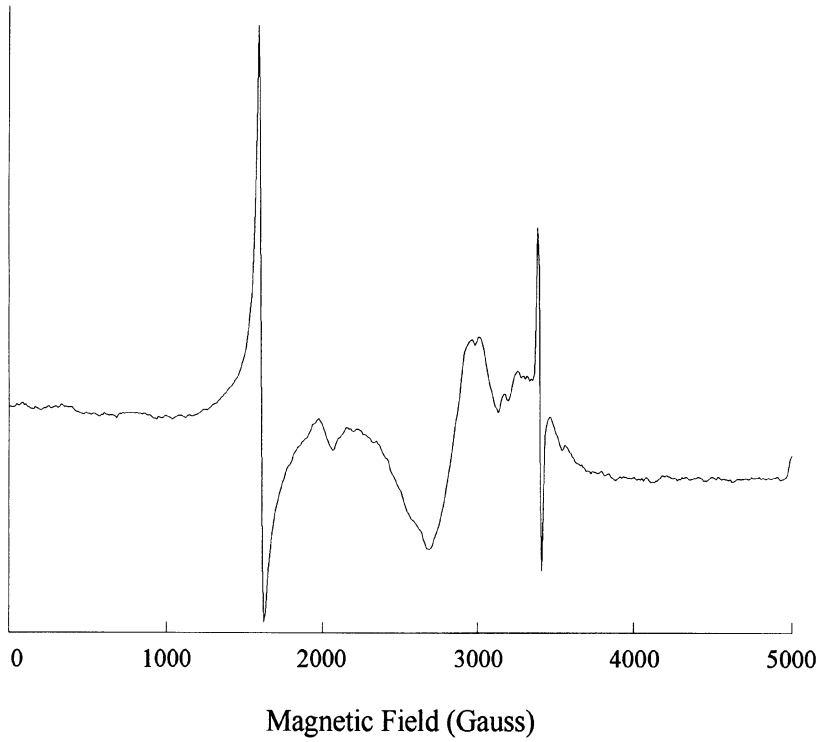

Figure 2. A wide field scan of the EPR spectrum of a glass-epoxy composite.

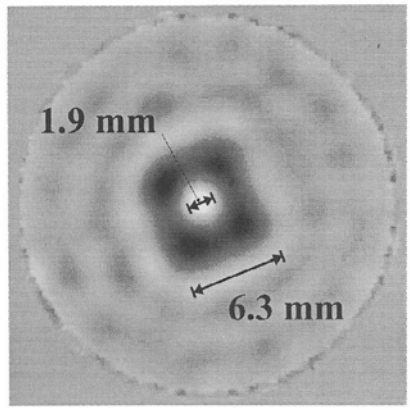

Figure 3. Reconstructed EPR two dimensional image of a rectangular glass epoxy composite sample containing a circular hole.

increasing the number of projections employed and by using advanced image post-processing techniques. These results indicates that good quality images are obtainable using native paramagnetic impurities in samples but that the resolution is generally degraded by the broadness of the signal.

A technique that can be employed for samples that have no intrinsic EPR signal or for cases where the intrinsic spectral features is unacceptably broad, is based on artificially doping the specimen with a paramagnetic substance. This technique was applied to a specimen of silica based ceramic. A sample of the porous ceramic was placed in a solution of DPPH dissolved in toluene. After allowing the solution to penetrate into the ceramic sample, the image shown on the left of Figure 4 was reconstructed from a series of 36 equally spaced projections spanning 180 degrees. A photograph of the sample is shown on the right of Figure 4 for comparison.

The EPRI image distinctly shows the outline of the sample with darker region near the corners. Since the technique is based on diffusion of the paramagnetic tracer into the sample, the image shows the depth of penetration of the paramagnetic material. Given the relatively slow diffusion of DPPH into this sample (the sample porosity is approximately 10%) over the period of exposure, only a sample outline is visible. Those regions closest to the edge have higher concentrations of DPPH and are darker, with the effect being magnified at the corners, given their proximity to two edges. This experiment shows the utility of the paramagnetic tracer technique for generating high quality images of normally EPR silent materials. In addition, a straightforward method for nondestructively measuring the porosity and diffusion coefficients of ceramic materials has emerged. By determining the depth of penetration of a paramagnetic tracer into the ceramic material for a given exposure time, the diffusion coefficient of the material can be determined. Also, the paramagnetic penetrant method can be exploited to image the depth distribution of surface cracks in many kinds of nonporous materials by following the evolution of the EPR image as a function of exposure time.

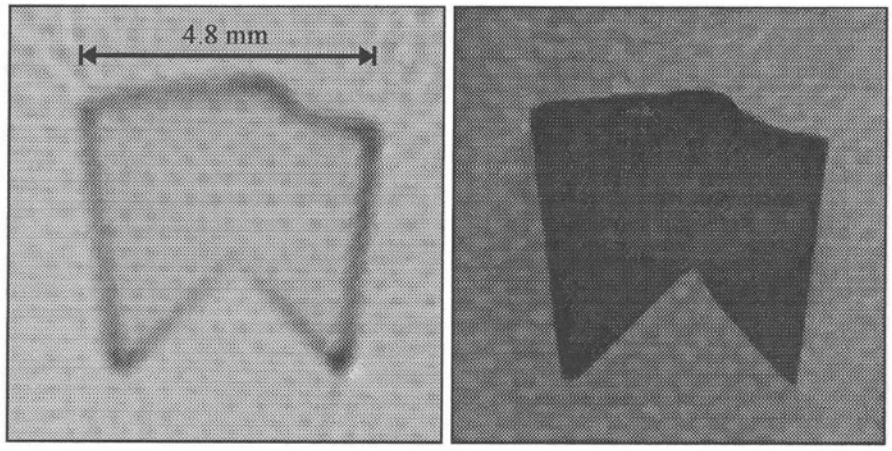

Figure 4. An example of a 2-D EPR image of a ceramic sample doped with an EPR sensitive penetrant. The image was created from 36 scans over 360 degrees. The image takes the form of an outline because the sample was placed in the DPPH solution only long enough for the penetrant to diffuse a short distance into the sample.

CONCLUSION

EPR imaging provides a natural tool for the investigation of damage in solid materials. Processes such as chemical reactions, mechanical stress and irradiation, which involve breaking chemical bonds, often generate unpaired electrons with narrow EPR lines that are suitable for imaging. Materials with unsatisfactory EPRI signals can be investigated using a paramagnetic doping technique.

High quality EPR images have been obtained for doped ceramic materials and undoped ceramics [1], polymers [1] and glass epoxy composites. Generally, the spectral characteristics of most intrinsic EPR resonances in undoped materials are not as narrow as the DPPH resonance line. Consequently, images derived from these features will suffer in resolution. However, many of these spectral lines are narrow enough to provide useful images, when image enhancement and deconvolution techniques are employed. The free radical penetrant technique may be used to derive a variety of information from solid state materials. Firstly, for porous materials the dopant may be allowed to completely diffuse into the sample, revealing such features as such as holes, cracks, or other inhomogeneities in a three-dimensional EPR image. Secondly, the time dependence of dopant penetration into the solid may be monitored using EPRI with a resultant nondestructive measurement of the diffusion coefficient of the material. Finally, for less porous materials the technique may be used to reveal flaws that allow the paramagnetic penetrant to pass into the sample. Future efforts will focus on increasing the resolution of the EPRI technique using more powerful field gradients and advanced image reconstruction and processing techniques.

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2. P. C. Lauterbur, Nature 242, 190-191 (1973); P. C. Lauterbur, IEEE Trans. Nucl. Sci. NS-26, 2802-2809 (1979).

3. DPPH (2, 2-Diphenyl-1-picrylhydrazyl) is a stable, solid-state free radical compound.